Enhancement of pesticide photo-Fenton oxidation at high salinities

María M. Micó [a,*], Jordi Bacardit [b], Jorge Malfeito [b], Carme Sans [a]

[a] Departament d'Enginyeria Química, Universitat de Barcelona, Martí i Franquès 1, 6th Floor, 08028 Barcelona, Spain
[b] ACCIONA Agua, S.A.U. Avda. de les Garrigues, 22, Parque de Negocios Mas Blau II, 08820 El Prat de Llobregat, Barcelona, Spain

ARTICLE INFO

ABSTRACT

The performance of the photo-Fenton reaction under high salinity conditions (up to $50\,mS\,cm^{-1}$) has been tested regarding the oxidation of two pesticides, imidacloprid and methomyl, in the shape of their commercial formulations. In opposition to what is commonly outlined in the literature, an enhancement in pesticides depletion has been found due to the positive participation of halogen radicals, $Cl^\bullet$. However, this beneficial effect does not improve organic carbon elimination but rather displays worse total organic carbon (TOC) depletion. This effect is most likely due to the hydroxyl radicals scavenging and the complexation of Fe^{3+} by chloride salts, which reduce the availability of reagents. Although salts/Fe^{3+} interaction was observed, Fe^{3+} interaction with the organic content was revealed as more relevant, especially for imidacloprid.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

1.1. Photo-Fenton process

Advanced oxidation processes (AOPs), which are based on the generation of very reactive and oxidizing free radicals, especially hydroxyl radicals, have been reported to be powerful oxidative techniques [1]. Among these processes, the homogeneous photo-Fenton reaction and the titanium dioxide-mediated heterogeneous photocatalytic treatment have recently shown great promise for the treatment of industrial wastewater [2,3] and the prevention of groundwater contamination of [4,5]. $HO^\bullet$ is a highly reactive transient specie that can rapidly oxidize most organic substances [6]; furthermore, catalytic behavior and light enhancement can improve its potentialities.

In the photo-Fenton reaction, the generation of hydroxyl radicals is achieved by the decomposition of hydrogen peroxide by means of the oxidation of dissolved ferrous ions, reaction (a), in the presence of UV light, which photo-reduces Fe^{3+}, reaction (b), thereby recovering Fe^{2+} and contributing to an additional pathway leading to a greater generation of free radicals in comparison to the dark Fenton reaction [7–9].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^\bullet + HO^- \quad \text{(dark Fenton)} \quad \text{(a)}$$

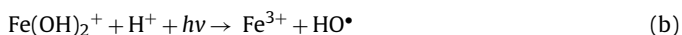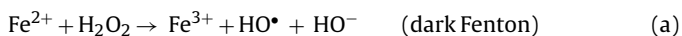$$Fe(OH)_2^+ + H^+ + h\nu \rightarrow Fe^{3+} + HO^\bullet \quad \text{(b)}$$

Photo-catalytic processes present several drawbacks in practical applications, such as the amount of chemicals needed and the pH 3 requirement (to prevent $Fe(OH)_3$ precipitation). However, photo-Fenton also has some advantages over heterogeneous catalysis. For instance, the employed reagents are harmless once the process is complete, and if Fe^{2+} working conditions meet reuse standards, there is no need for catalyst separation and recovery. In addition, solar light could also be a suitable source of radiation for the process, which makes it optimum for outdoor installation, especially in rural areas, which in turn reduces both costs and risks [10–12].

Extensive work has addressed the photo-Fenton reaction as applied to pesticides decontamination [8,13–17]. Studies have established this process as a suitable treatment for bio-recalcitrant pollutants. Most of this research has been performed in countries with rural regions under high hydric stress where the reuse of even agricultural water is required. The most important characteristics of this water are their content of salts, mainly chlorides, nitrates and sulfates, a certain amount of BOD and COD, traces of pesticides, and inert ingredients that comprise commercial products and their degradation by-products.

The photo-Fenton reaction has been widely studied from all possible perspectives; although notable contributions can be found [18–20], a weakness of the extant research is the scarce study of two important aspects that the present work addresses: this reactions' performance with commercial formulations versus moderate/high salinities. In the recycling hydroponic system envisaged in this study the effluents might function under either condition.

* Corresponding author. Tel.: +34 934021313; fax: +34 934021291.
  E-mail address: mmarmico@angel.qui.ub.es (M.M. Micó).

1.2. Hydroponics scenario

Hydroponics is a culture method conducted in a soil-less environment that is usually installed inside greenhouses of varying sophistication. The nutrient source is provided directly to the roots by means of a flowing solution. These systems allow for the control of nutrients given to the plants, thereby assuring the nutrient sources' nutritive and sanitary qualities [21]. Their advantages include their high production per unit area compared to soil cultures and the independence of external climate conditions. Both of these factors are particularly interesting for extreme climate regions, which are often present in developing countries in need of higher productivity.

Hydroponics typically work as closed systems, preventing the leaching of chemicals into ground or surface water and enabling the recycling of the nutrient effluent as many times as needed; while the increasing concentration on salts and pesticides does not harm the crops. It is considered an efficient technique of saving water from which regions such as Spain, where water scarcity provokes the overexploitation of wells and their consequent salinization by seawater intrusions [22] can benefit. In particular, an area that may take profit of is Spanish struggling South Basin, where the use of protected agriculture [23] is already extensive and where technification by hydroponics has not yet been widely utilized as a way of economizing water.

Despite the positive aspects of recycling after a number of rounds, the effluent cannot be directly discharged to the environment due to its enriched salt content and pesticide-derived products. Treatment is necessary to recondition the effluent prior to sending it back to the system or for it to meet the sewage system's standards.

1.3. Objectives

The aim of this work is to study the suitability and performance of the photo-Fenton reaction for degrading a mixture of two commercial pesticide formulations based on methomyl and imidacloprid in the presence of high salinity. The working scenario is a simulated hydroponic greenhouse where the effluents can be reused several times as a semi-closed system until they reach a conductivity threshold, at which point the flows are diverted to treatment once they have high concentrations of salts, pesticides and related organics.

2. Experimental

2.1. Photo-Fenton reaction

The photo-Fenton reaction was carried out in a 2 L jacketed stirred vessel with three 8 W black light lamps (λ_{max} = 365 nm) axially arranged to the reactor. This device was connected to a thermostatic bath that permitted the experiments to evolve at a controlled temperature of 21 °C. A more detailed description of the device and the procedure can be found elsewhere [7]. The pH was set to 2.7 (optimum for the equilibrium [Fe^{2+}]/[Fe^{3+}] to achieve its highest ratio) at the beginning of the reaction with H$_2$SO$_4$ (Panreac) diluted solution. This value was monitored during the process and kept constant between 3 and 2.5. Except for the 60 min experiments, all of the trials were carried out until reaching the total consumption of hydrogen peroxide. Every set and every sample was withdrawn and then quenched with NaHSO$_3$, 40% (w/v) (Panreac) to remove the remaining hydrogen peroxide.

2.2. Chemicals

Methomyl and imidacloprid were chosen as target compounds due to their extended application in horticulture. They present different chemical structure and properties. While methomyl is an N-carbamate (Fig. 1a), imidacloprid is a neonicotinoid (Fig. 1b), a third-generation pesticide. Commercial formulations of both products were used with no further purification. Tomilo-20 L was the carbamate source and Kohinor the neonicotinoid's; 200 g L^{-1} of active principle in each product. Both were obtained from Aragonesas Agro S.L. (Spain).

KNO$_3$ with no antipackaging, CaCl$_2$•2H$_2$O, NH$_4$Cl, MgSO$_4$•7H$_2$O, NaHCO$_3$, NaCl, and CaSO$_4$•2H$_2$O were used for simulating the salinity content. FeSO$_4$•7H$_2$O was the source for ferrous ions, and hydrogen peroxide was dispensed as a commercial solution of 30% (w/v). All of these substances were purchased from Panreac. Deionized water was used to prepare every solution.

2.3. Chemical analyses

Pesticides depletion in each experiment was monitored using high performance liquid chromatography with a photodiode array detector. The column used was a Mediterranean Sea18, 5 μm 25 cm × 0.46 cm (Teknokroma). The mobile phase, composed of a mixture of water and acetonitrile (both from Merck) (60:40), was delivered at a flow rate of 1 mL min^{-1}. In the cases with higher salinity content, a peak related to a NaCl-masked methomyl peak; therefore, another method was used, having a mobile phase composed of 2.5 mL of 80% H$_3$PO$_4$, 25 mL of methanol diluted to 500 mL with milli-Q water. In this case, the flow was 0.7 mL min^{-1}. The wavelength of the UV maximum absorbance was 232.5 nm for methomyl, while for imidacloprid, it was 269 nm. Dissolved organic carbon was also monitored in the shape of TOC, total organic carbon, by a Shimatzu TOC-VCSN TOC analyzer. Dissolved ferrous ion (together with total iron) and hydrogen peroxide were followed by spectrophotometric methods [24,25]. 1,10-Phenantroline was purchased from Aldrich, while sodium acetate, acetic acid, and ascorbic acid were purchased from Panreac, as were NH$_4$VO$_3$ and H$_2$SO$_4$.

2.4. Experimental plan

The photo-Fenton reaction was tested with different salinity conditions, from no salts to a concentration of 42.13 g L^{-1}. Table 1 shows the averaged parameters of each type of effluent, grouped in Set A, before chemical treatment. The added salts were determined according to the previous literature regarding the typical minerals needed by crops and soilless cultures [26–28]. In the case of A1, only the essential salts for crop nutrition were added, while in A2, A3, and A4, the principal species that caused salinity problems (NaCl and CaSO$_4$) were also added. While the conductivities of A1 and A2 represent intermediate points of conductivity that could be still used in the hydroponic system, A3 accounts for the threshold salinity limit, the extent to which plants can be forced, according to Fornes and Montesano [29,30]. A4 represents a highly saline effluent closed to the conductivity of seawater. The aim of this experiment was to analyze the extension of the salinity effect under extreme conditions.

The photo-Fenton reaction was carried out with initial reagents concentrations of 10 mg L^{-1} of ferrous iron (FeSO$_4$) and 100 mg L^{-1} of hydrogen peroxide. These values were chosen according to previous experiments in which these concentrations enabled the total depletion of 20 mg L^{-1} of imidacloprid without any salt [8]. All experiments, except otherwise is noted, were carried out until hydrogen peroxide was totally consumed.

Samples of the photo-Fenton reactor were withdrawn along the reaction for this set, and successive experiments and the following
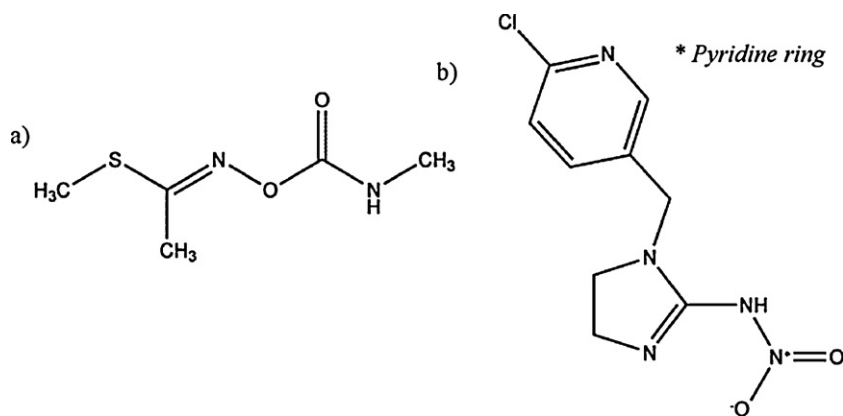
Fig. 1. (a) and (b) molecular structures of methomyl and imidacloprid, respectively.

species concentrations were analyzed: pesticides, total organic carbon, dissolved ferrous iron and dissolved total iron, and hydrogen peroxide.

3. Results and discussion

3.1. Effect of salinity on pesticide and organic matter depletion

Methomyl degradation within the mixture of two pesticides is represented in Fig. 2, where changes in elimination curves behavior can be observed according to the conductivity of the effluents.

As seen, the elimination of methomyl is complete in any case at the end of the experiment. For higher salinities, faster degradations of the carbamate were achieved. The lowest conductivity effluent shows a slight decrease in the elimination rate, compared to the control type. When salinity achieves $5\,\mu S\,cm^{-1}$, the oxidation seems to go faster and slightly increases, doubling the salt

content. The degradation pattern is also different. For lower salinities, the oxidation begins more slowly and increases its rate after 1 h of treatment, while for the highest conductivities; the degradation is quite rapid from the beginning.

In the case of imidacloprid performance, Fig. 3 illustrates how, for every conductivity, the depletion of imidacloprid is complete.

It is notable that despite the concentration of salts, imidacloprid is degraded in a similar pattern and rate, while a more rapid oxidation step in the first minutes of the reaction and subsequent slowing until total elimination have been reported elsewhere, [31,32], even using different oxidation technologies [33].

Comparing pesticide elimination to H_2O_2 consumption for the extreme experiments, as depicted in Fig. 4, it is shown how the tendencies are different depending on the salt content. The process seems to be slower in the absence of salts, where the decomposition of the hydrogen peroxide follows the same pattern as methomyl elimination; the latter is noticeably slower than imidacloprid depletion. Nevertheless, Fig. 4b represents how, for experiment A4,

Table 1
Summary of salts concentration and conductivity of each experiment performed.

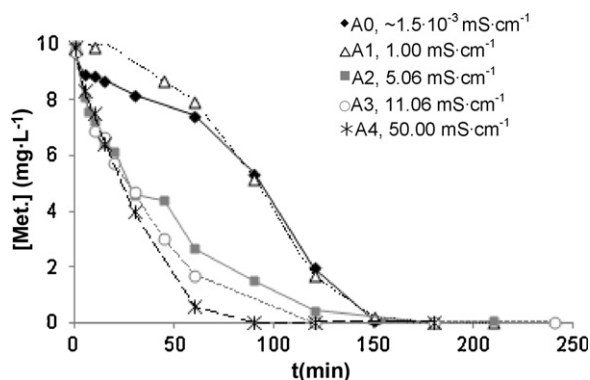|	Specie	Salts conc. (g L^{-1})	Total salts conc. (g L^{-1})	Conductivity (mS cm^{-1})	[Cl−] (M)
Set A, mixture (10 mg L^{-1} imidacloprid, 10 mg L^{-1} methomyl, 44 mg L^{-1} TOC$_0$)					
A0	Non added salts			$\sim 1.5 \times 10^{-3}$	0
A1	KNO$_3$	0.60	0.9	1.00	2×10^{-3}
	CaCl$_2$	0.10			
	NH$_4$Cl	0.05			
	MgSO$_4$	0.05			
	NaHCO$_3$	0.10			
A2	KNO$_3$	0.60	4.6	5.06	0.05
	CaCl$_2$	0.10			
	NH$_4$Cl	0.05			
	MgSO$_4$	0.15			
	NaHCO$_3$	0.10			
	NaCl	3.00			
	CaSO$_4$	0.60			
A3	KNO$_3$	1.25	9.05	11.06	0.1
	CaCl$_2$	0.10			
	NH$_4$Cl	0.05			
	MgSO$_4$	0.30			
	NaHCO$_3$	0.10			
	NaCl	6.00			
	CaSO$_4$	1.25			
A4	KNO$_3$	1.25	42.13	50.00	0.6
	CaCl$_2$	0.10			
	NH$_4$Cl	0.05			
	MgSO$_4$	0.90			
	NaHCO$_3$	0.08			
	NaCl	36.00			
	CaSO$_4$	3.75			

Fig. 2. Concentration of methomyl along the process. The reaction reached completion when all of the hydrogen peroxide was consumed.
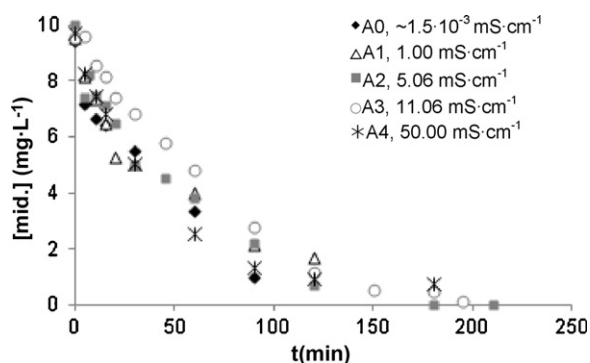

Fig. 3. Concentration of imidacloprid along the reaction, Set A. The reaction was finished when all of the hydrogen peroxide was consumed.
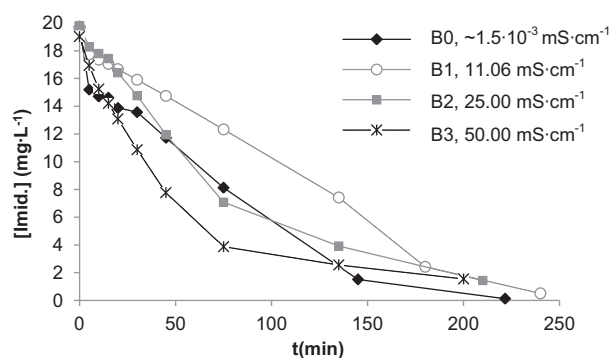

Fig. 5. Concentration of imidacloprid along the reaction, Set B. The reaction was complete when all of the hydrogen peroxide was consumed.
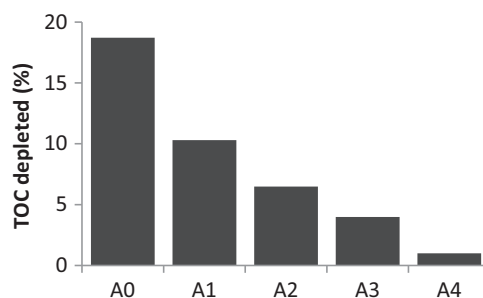

Fig. 6. Total percentage of TOC depletion for Set A experiments.

the carbamate consumption is somewhat faster than the degradation of the other target compound and how peroxide was also consumed at a higher rate.

Higher salinity experiments were performed with 20 mg L^{-1} of the neonicotinoid as the single target compound, with the same concentration in reagents and the same salt proportions. Experimental conditions for Set B are summarized in Table 2.

As observed in Fig. 5, effectively, the influence of salt increases for imidacloprid. Apparently, the lowest salinity has a negative influence on the degradation of imidacloprid, while higher salinities seem to cause faster degradation, as occurred in the presence of methomyl. However, the depletion achieved is reduced by almost 10% for the two highest values of conductivity.

The weak but positive impact that salinity seems to have in the case of imidacloprid for Set B, together with the noticeable improvement of the methomyl degradation rate in the presence of salts, undermines the notion of inorganic ions, such as NO_3^-, SO_4^{2-} and Cl^-, [19,32–35] provoking interferences in the photo-Fenton reaction, implying lower oxidation results, as has been reported in

previous literature. On one hand, these anions could be blamed for a scavenging effect of hydroxyl radicals [18,19,36]; for chloride, these effects were established to be noticeable above 0.01 M Cl^- [37]. On the other hand, these anions have also been found to cause complexation with dissolved Fe(III), forming less photoactive species [18].

The influence of the anions over hydroxyl radicals could explain the faster hydrogen peroxide degradation observed in Fig. 4b, while the combination of both effects could justify the low TOC diminishment at the end of the process. Although depletion is low even in the experiments without any salt, conductivity seems to clearly affect the mineralization of the organic load, reducing the TOC [38] elimination while conductivity increases.

Fig. 6 presents those values. Even in the most beneficial case, the total TOC removal is quite low compared to the total degradation that pesticide content achieves. As proposed by Kavitha and Oturan [39,40], the formation of hardly oxidizable by-products, such as short chain carboxylic acids, which are refractory to radical oxidation, deters TOC removal. Although higher salinity seems not to affect the depletion of the pesticides themselves, it hinders the oxidation of the organic content, confirming what the previous literature found, most likely due to the lack of availability of hydroxyl
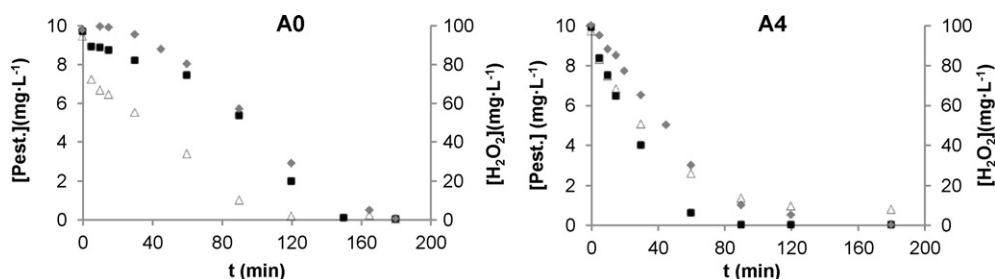

Fig. 4. (a and b) Comparison between pesticides depletion and hydrogen peroxide consumption for extreme cases. (■) methomyl, (△) imidacloprid, (♦) hydrogen peroxyde. A0, 1.5×10^{-3} mS cm^{-1}, A4, 50.0 mS cm^{-1}.

Table 2
Summary of salts concentration and conductivity of each experiment performed as set B.

Set B, mixture ($20 \, mg \, L^{-1}$ imidacloprid, $0 \, mg \, L^{-1}$ methomyl, $41 \, mg \, L^{-1} \, TOC_0$)				
	Specie	Salts conc. ($g \, L^{-1}$)	Total salts conc. ($g \, L^{-1}$)	Conductivity ($mS \, cm^{-1}$)
B0	Non added salts			$\sim 1.5 \times 10^{-3}$
B1	KNO_3	1.25	9.05	11.06
	$CaCl_2$	0.10		
	NH_4Cl	0.05		
	$MgSO_4$	0.30		
	$NaHCO_3$	0.10		
	$NaCl$	6.00		
	$CaSO_4$	1.25		
B2	KNO_3	1.25	24.15	25.00
	$CaCl_2$	0.10		
	NH_4Cl	0.05		
	$MgSO_4$	0.90		
	$NaHCO_3$	0.10		
	$NaCl$	18.00		
	$CaSO_4$	3.75		
B3	KNO_3	1.25	42.13	50.00
	$CaCl_2$	0.10		
	NH_4Cl	0.05		
	$MgSO_4$	0.90		
	$NaHCO_3$	0.08		
	$NaCl$	36.00		
	$CaSO_4$	3.75		

radicals and Fe^{3+} ready to be returned to Fe^{2+}; these conditions could promote the formation of these recalcitrant substances.

Additional sets of experiments with less-complex matrices were performed. In all of them, chloride was most suspected of influencing the photo-Fenton reaction, as it was the most significant contributor to the total conductivity of the effluents. As methomyl seems to suffer more acute effect on degradation, the following study was primarily focused on this pesticide. The remaining pesticide was measured along a 60 min photo-Fenton reaction; to which three solutions were submitted (these experiments were stopped before all the H_2O_2 was consumed). All of them were prepared with $20 \, mg \, L^{-1}$ of methomyl and $10 \, mg \, L^{-1}$ of Fe^{2+}. No salt was added to the first solution, while $15.8 \, g \, L^{-1}$ of KCl was added to the second solution and $18.5 \, g \, L^{-1}$ of KNO_3 to the third solution to obtain two solutions with the same electric conductivity, $25 \, mS \, cm^{-1}$, and compare the effect of both anions. No conclusions about TOC depletion could be made in these experiments due to the low values obtained even for the solution without salts. Nevertheless, regarding pesticide elimination, Fig. 7 shows how the presence of high chloride concentration in fact improves the degradation of the carbamate in comparison to the nitrate solution and the

solution without any salt, which both had similar behaviors, indicating that chloride plays a special role in promoting the degradation of the pesticide. It was concluded that Cl^- was the main contributor to enhanced pesticide depletion.

Photo-Fenton reactions were also performed over a mixture of pesticides in a solution with no salts and a solution with $15.8 \, g \, L^{-1}$ of KCl, both spiked with $20 \, mg \, L^{-1}$ of methomyl and $20 \, mg \, L^{-1}$ of imidacloprid (with $10 \, mg \, L^{-1}$ of Fe^{2+}, each). Comparing Figs. 7 and 8a (different scale), it can be seen how the depletion is higher for methomyl with or without chlorides added but lower in the presence of imidacloprid. This finding is most likely due to the higher quantity of initial organic content in these experiments. Nevertheless, Fig. 8a itself depicts how depletion of the methomyl is clearly improved by the presence of halide salts in comparison to the experiments without them, while Fig. 8b shows an insignificant influence of the halide in imidacloprid elimination. Both facts confirm what was seen in Figs. 2 and 5, respectively. No conclusion could be drawn from TOC depletion results due to their low value.

As stated above, OH· scavenging and Fe^{3+} complexation could be attributed to halide ions, chloride in this case, which may have a negative effect even on pesticides. Nevertheless, it is also noted in the literature that under certain conditions, the reactive halogen species that is derived from hydroxyl scavenging can be more than a HO· sink and may participate in contaminant destruction [41]. Reactions (c)–(f) [18,38] represent the processes taking place between the hydroxyl radicals and the halide anions.

$$HO^\bullet + X^- \rightleftharpoons XOH^{\bullet-} \qquad (c)$$

$$XOH^{\bullet-} + H^+ \rightleftharpoons X^\bullet + H_2O \qquad (d)$$

$$XOH^{\bullet-} + X^- \rightleftharpoons X_2^{\bullet-} + OH^- \qquad (e)$$

$$X^\bullet + X^- \rightleftharpoons X_2^{\bullet-} \qquad (f)$$

While halogen radical anions, $X_2^{\bullet-}$, are generally less reactive than hydroxyl radicals, the magnitudes of halogen atoms $X^\bullet$ rate constants with organic compounds are comparable to those for $OH^\bullet$. This monoatomic species, favored by acidic pH, can react by one-electron oxidation by H-abstraction and by addition to unsaturated C–C bonds, while hydroxyl radical oxidation is mostly based on the latter [41].
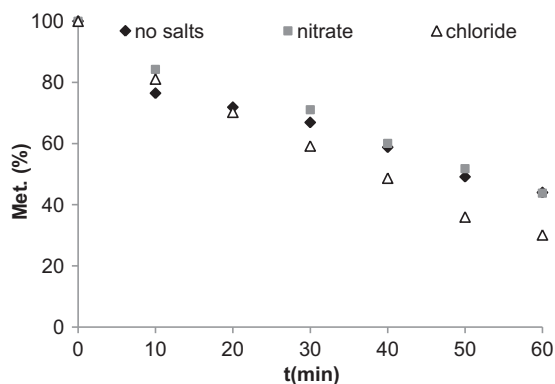

Fig. 7. Evolution of methomyl in different salinity conditions; no salts, negligible conductivity; with chloride or nitrate, $C = 25 \, mS \, cm^{-1}$, $[Met.]_0 = 20 \, mg \, L^{-1}$, $TOC_0 = 46 \, mg \, L^{-1}$.
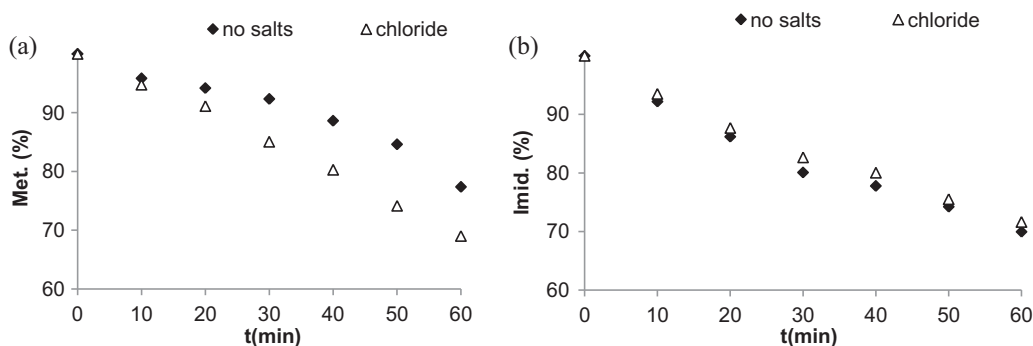
Fig. 8. (a and b) Evolution of the pesticides in different salinity conditions; no salts, negligible conductivity; chloride, 25 mS cm^{-1}; [Met.] = [Imid.] = 20 mg L^{-1}, TOC$_0$ = 83 mg L^{-1}.

Accordingly, the participation of this type of radicals could justify the improvement of methomyl and imidacloprid depletion and even the changes in their profiles. Furthermore, due to the molecular formula of methomyl, chloride radicals could promote the formation of extremely nucleophilic compounds based on its chlorosulfenyl group. These substances could collaborate in the oxidative process. In the case of imidacloprid, the improvement is not so obvious due to its molecular structure, mainly its pyridine ring, which tends to stabilize any type of radical instead of promoting the expected chain reactions. From the point of view of TOC depletion, on one hand, the reactive halides themselves are not powerful enough to lead to mineralization; on the other hand, halide anions seem to have a negative effect, most likely due to the scavenging effect over hydroxyl radicals or the complexation of Fe(III) that hinders its recycling.

3.2. Effect of salinity on iron catalyst

The influence of inorganic ions was also explored by analyzing the presence of dissolved ferrous iron along the photo-Fenton reaction, as was reflected in Fig. 9, where results for Set A are represented.

A general behavior can be distinguished among the different experiments. Ferrous ion suffers an extreme decrease when the hydrogen peroxide is added to the media, no matter the conductivity of the effluent, and its concentration is kept low during the process until 70–80% of the peroxide is consumed, coinciding with the lowest remaining concentrations of the pesticides. At this point, a certain level of recovery is detected with respect to the salt content: the strongest recovery is registered for experiment A0 and the weakest for A4.

Inorganic ions are known to exert some coordinating effect over ferric ions [18], with the formation of thermodynamically favored complexes such as FeCl^{2+}, FeCl$_2^+$, and Fe[(SO)$_4$]$_2^-$ reducing the capability of the photo-Fenton reaction to recycle ferrous iron
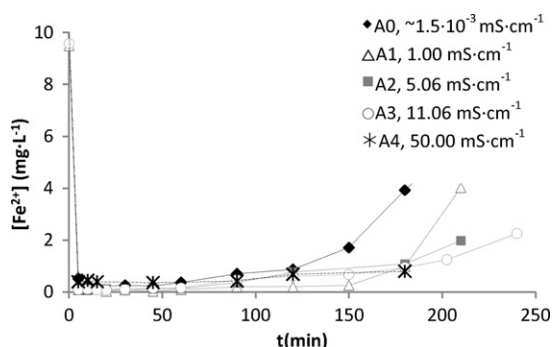
[42]. In fact, the complexation of iron by chloride and sulfate ions could be primarily responsible for the diminishment of the process' efficiency [35], depending on its concentration. Complexation is reflected on the different recovery rates in the final phases of the reaction.

Focusing on the decrease of Fe^{2+} at the beginning of the reaction, when hydrogen peroxide is added, there is a rapid interaction between this reagent and Fe^{2+} dissolved ions, causing their oxidation into Fe^{3+}, according to the well-known Fenton reaction, Eq. (1) in Fig. 10. Once ferrous iron is converted into Fe(III), apart from the formation of photoactive aquo-complexes, reaction (2) is favored in acidic pH [38]; in the presence of H$_2$O$_2$, the equilibriums detailed in reactions (3) and (4) are established almost instantly [18].

In the absence of any other complexing agents, this complexation is reverted by the reduction of ferric ion, reactions (5) and (6) [18], in which the complex breaks into a ferrous ion and radicals. Nevertheless, these processes have very low reaction rates in comparison to the photo-enhanced reaction (7), which is supposed to be the main path for the recovery of Fe^{2+} in the photo-Fenton process [43,44]. This reaction does not require the participation of hydrogen peroxide and constitutes an additional means to generate hydroxyl radicals [18]. According to the catalytic and cyclic character of the photo-Fenton reaction, a near-total recovery of ferrous iron was anticipated in the process, far from what was actually observed.

All of these reactions are expected to happen constantly throughout the photo-Fenton process; however, there may be, as in this case, other complexing reactions that disable Fe^{3+} from participating in this cycle as efficiently as expected.

No interactions between the phytosanitary products themselves and Fe^{2+} were detected, as no initial depletion of this specie was observed previous to the addition of hydrogen peroxide. However, it is accepted that apart from inorganic ions, Fe(III) may also complex with certain organic compounds [44], especially those acting as polydentate ligands, which would explain the low levels of dissolved Fe(II) until nearly the end of the trials. Therefore, particular experiments were carried out to determine whether the commercial formulations of each pesticide could prevent Fe^{3+} from being

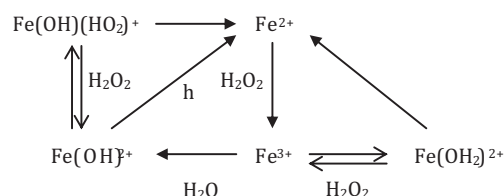**Fig. 9.** Progress of dissolved Fe^{2+} versus reaction time for Set A.

Fig. 10. Simplified diagram of iron cations chemistry. Reactions are not balanced. Reaction (2) is representative of the several reactions that take place between Fe(III) and water.
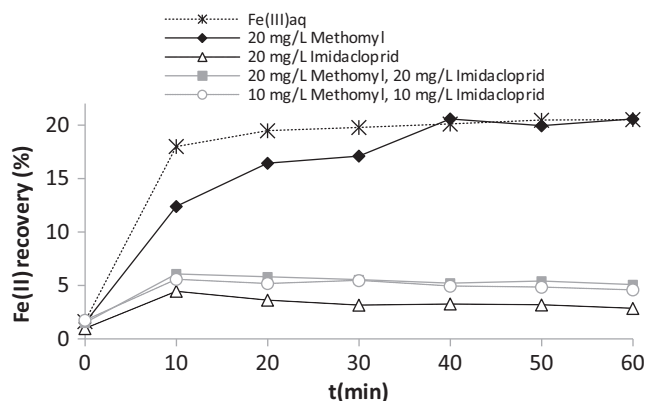
Fig. 11. Recovery of dissolved Fe(II) along the exposition to UV light of Set E experiments, pH = 2.7.

photo-reduced. The experiments, depicted in Fig. 11, consisted of Fenton-like reactions in which different solutions of $FeCl_3$ ($[Fe^{3+}]_0 = 10\,mg\,L^{-1}$) and commercial pesticides ($[Met.] = 20\,mg\,L^{-1}$ and/or $[Imid.] = 20\,mg\,L^{-1}$) were submitted to UV-light for 60 min, with no addition of hydrogen peroxide, in the same reactor where previous photo-Fenton experiments were performed. A comparison of the photo-reduction of Fe(III) into Fe(II) in a solution without the presence of any pesticides was established.

It can be observed that the effect of UV light is the ability to convert more than 20% of the Fe(III) into Fe(II) in a solution with only $FeCl_3$; this recovery is also achieved in the presence of methomyl. In contrast, the imidacloprid experiments showed a notably high negative effect by this pesticide or its inert ingredients in the photo-reduction of ferric iron, even in the case of the mixture with methomyl, in which the influence of imidacloprid overcame the neutral effect of the carbamate, corroborating what was observed for set A experiments.

Furthermore, Fig. 12 shows the evolution of ferrous iron in contrast with the pesticide depletion. It depicts how the imidacloprid concentration did not diminish, while methomyl slightly decreased as the percentage of dissolved Fe(II) increased. Because previous experiments proved that no photolysis of methomyl is caused at working wavelengths, the depletion of the pesticide is likely due to the hydroxyl radicals generated by the photo-reduction of Fe(III) complexes. As imidacloprid or its inert ingredients seem to block iron reduction, a low amount of hydroxyl radicals are generated

and, consequently, extremely low depletion of imidacloprid was observed.

The results indicate that methomyl or its inert ingredients (mainly dibasic esters) can complex ferric iron of a certain grade [45]; the recovery is lower than for the experiment without organics, but they are either easily photo-decarboxyled or oxidized by the radicals generated in the iron photo-reduction, freeing Fe^{3+} for its recycling. On the other hand, even in the case of salts' absence, imidacloprid commercial formulation prevents Fe(III) photo-reduction. No complexing effect can be attributed to the organic solvents that the commercial formulation contains, dimethyl sulfoxide and propylene carbonate. Instead, there is an imidacloprid pyridine ring, Fig. 1b, that provokes the chelating effect over ferric ions [46]. This ring is unharmed during the first stages of the degradation of the compound [32]. However, with the evolution of the reaction, this cycle is also decarboxyled and decomposed by the produced radicals, promoting the regeneration of a slightly higher concentration of Fe(II) near the end of the process.

Apparently, in Set A experiments, ferrous iron evolution along the reaction followed three stages. The first consisted of an extreme drop due to the addition of H_2O_2, while the second step was related to the nature of the present pesticides. Both substances, together with Tomilo-20 L inert ingredients but mainly imidacloprid and its by-products, complexed Fe(III) until radical reactions degraded them sufficiently to cause the recovery of Fe(II) that took place in the third stage depending on the salt content and inorganic complexes generated. Not even in the A0 case was the Fe(II) upturn complete; therefore, it may be assumed that although the pesticides were consumed, some by-products still prevented ferric ions from being recycled.

4. Conclusions

The photo-Fenton reaction was revealed to be an efficient way to oxidize mixtures of imidacloprid and methomyl, even for salt contents and conductivities close to those of seawater.

Contrary to what is commonly found in the literature, chloride anions seem to favor the degradation of both target compounds, especially methomyl (even in a mixture with imidacloprid). This enhancement can be attributed to the generation of halide radical species, $X^\bullet$, that contribute to the degradation of the pesticides by new reaction paths. However, TOC depletion is not enhanced but worsened, potentially due to the global effect of chlorides through hydroxyl radicals scavenging and the complexation of Fe(III) by chloride and sulfate salts. It can be concluded that salinity has a particularly positive effect on the decomposition of the pesticides, which cannot be perceived by taking into account global organic matter depletion that is worsened by the presence of inorganic ions.

Available Fe(II) should be taken into account for future optimizing works due to the possible complexation of Fe^{3+} by the oxidizing substances, depending on their molecular structure. In this case, the imidacloprid pyridine ring is suspected to complex a notable amount of Fe(III), while the effect of methomyl and its inert ingredients is minimal.

Additionally, chlorides have been proved to influence ferrous ion recovery, although, in this case, their effect was overshadowed by the organic ferric complexes until the final minutes of the reaction. In those moments, the direct influence of salinity could be seen in the different rates of Fe^{2+} recovery, which were higher for the lower conductivity values.

Further work should be performed to test whether the participation of chloride radicals in the oxidation of organic matter could promote the generation of organochlorinated substances. Further studies should also assess the viability of a subsequent biological treatment loaded with photo-Fenton processed salty effluents to
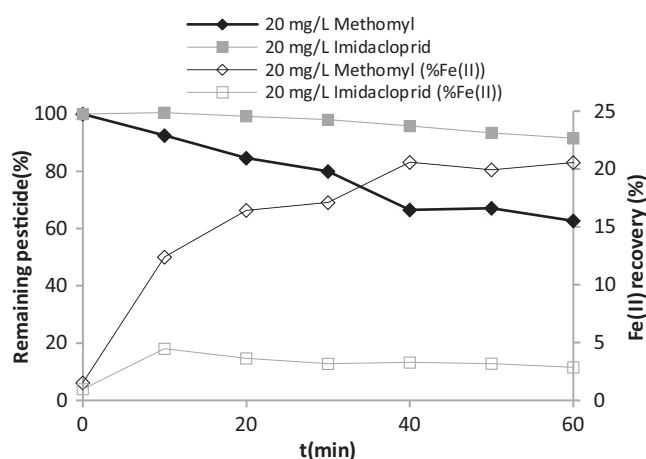

Fig. 12. Comparison between the depletion of pesticides and Fe(II) recovery along the exposition to UV light.

address the remaining organic content not degraded in the photo-Fenton process.

Acknowledgments

The authors are grateful to ACCIONA Agua and CDTI (Ministry of Industry, Spanish Government) for their financial support through the CENIT-MEDIODIA project. They also extend gratitude to Olga Carreño of the University of Barcelona for her help and collaboration.

References

[1] M.I. Badawy, F.E. Gohary, M.Y. Ghaly, M.E.M. Ali, Journal of Hazardous Materials 169 (2009) 673–679, http://dx.doi.org/10.1016/j.jhazmat.2009.04.038.

[2] M. Pera-Titus, V. García-Molina, M.A. Baños, J. Giménez, S. Esplugas, Applied Catalysis B: Environmental 47 (2004) 219–256, http://dx.doi.org/10.1016/j.apcatb.2003.09.010.

[3] M.S. Lucas, J.A. Peres, C. Amor, L. Prieto-Rodríguez, M.I. Maldonado, S. Malato, Journal of Hazardous Materials 225–226 (2012) 173–181, http://dx.doi.org/10.1016/j.jhazmat.2012.05.013.

[4] V.J.P. Vilar, E.M.R. Rocha, F.S. Mota, A. Fonseca, I. Saraiva, R.A.R. Boaventura, Water Research 45 (2011) 2647–2658, http://dx.doi.org/10.1016/j.watres.2011.02.019.

[5] R. Zhao, J.T. Novak, C.D. Goldsmith, Water Research 46 (2012) 3837–3848, http://dx.doi.org/10.1016/j.watres.2012.04.022.

[6] R.G. Zepp, B.C. Faust, J. Hoigné, Environmental Science & Technology 26 (1992) 313–319, http://dx.doi.org/10.1021/es00026a011.

[7] O. González, C. Sans, S. Esplugas, Journal of Hazardous Materials 146 (2007) 459–464, http://dx.doi.org/10.1016/j.jhazmat.2007.04.055.

[8] M.M. Micó, J. Bacardit, C. Sans, Water Science and Technology 62 (2010) 2066–2074, http://dx.doi.org/10.2166/wst.2010.522.

[9] H. Kušić, N. Koprivanac, A.L. Božić, I. Selanec, Journal of Hazardous Materials 136 (2006) 632–644, http://dx.doi.org/10.1016/j.jhazmat.2005.12.046.

[10] A. Zapata, I. Oller, E. Bizani, J.A. Sánchez-Pérez, M.I. Maldonado, S. Malato, Catalysis Today 144 (2009) 94–99, http://dx.doi.org/10.1016/j.cattod.2008.12.030.

[11] C. Mendoza-Marín, P. Osorio, N. Benítez, Journal of Hazardous Materials 177 (2010) 851–855, http://dx.doi.org/10.1016/j.jhazmat.2009.12.111.

[12] A. Bernabeu, S. Palacios, R. Vicente, R. Vercher, S. Malato, A. Arques, A.M. Amat, Chemical Engineering Journal (2012), http://dx.doi.org/10.1016/j.cej.2012.05.056.

[13] A.K. Abdessalem, N. Bellakhal, N. Oturan, M. Dachraoui, M.A. Oturan, Desalination 250 (2010) 450–455, http://dx.doi.org/10.1016/j.desal.2009.09.072.

[14] S. Navarro, J. Fenoll, N. Vela, E. Ruiz, G. Navarro, Chemical Engineering Journal 167 (2011) 42–49, http://dx.doi.org/10.1016/j.cej.2010.11.105.

[15] A. Tomašević, E. Kiss, S. Petrović, D. Mijin, Desalination 262 (2010) 228–234, http://dx.doi.org/10.1016/j.desal.2010.06.019.

[16] I. Michael, E. Hapeshi, V. Osorio, S. Perez, M. Petrovic, A. Zapata, S. Malato, D. Barceló, D. Fatta-Kassinos, Science of the Total Environment 430 (2012) 167–173, http://dx.doi.org/10.1016/j.scitotenv.2012.05.003.

[17] E. Brillas, I. Sirés, M.A. Oturan, Chemical Reviews 109 (2009) 6570–6631.

[18] J.J. Pignatello, E. Oliveros, A. MacKay, Critical Reviews in Environmental Science & Technology 36 (2006) 1–84, http://dx.doi.org/10.1080/10643380500326564.

[19] J. Bacardit, J. Stötzner, E. Chamarro, S. Esplugas, Industrial and Engineering Chemistry Research 46 (2007) 7615–7619.

[20] M. Rodriguez, V. Sarria, S. Esplugas, C. Pulgarin, Journal of Photochemistry and Photobiology A 151 (2002) 129–135, http://dx.doi.org/10.1016/S1010-6030(02)00148-X.

[21] M.D. Gómez-López, J.P. Fernández-Trujillo, A. Baile, Scientia Horticulturae 110 (2006) 67–78.

[22] Ministerio de Agricultura, Alimentación y Medioambiente.2012 4.

[23] A. Sánchez-Picón, J.A. Aznar-Sánchez, J. García-Latorre, Journal of Arid Environments 75 (2011) 1360–1367, http://dx.doi.org/10.1016/j.jaridenv.2010.12.014.

[24] Internacional Organization for Standarization, ISO 6332:1982 (1982).

[25] R.F.P. Nogueira, M.C. Oliveira, W.C. Paterlini, Talanta 66 (2005) 86–91.

[26] J.J. Magán, M. Gallardo, R.B. Thompson, P. Lorenzo, Agricultural Water Management 95 (2008) 1041–1055, http://dx.doi.org/10.1016/j.agwat.2008.03.011.

[27] A. Siber, A. Bal-Tal, in: M. Raviv, J.H. Lieth (Eds.), Soilles Cuture: Theory and Practice, Elsevier, Oxford, 2008, pp. 291–342.

[28] D. Massa, L. Incrocci, R. Maggini, C. Bibbiani, G. Carmassi, F. Malorgio, A. Pardossi, Environmental Modelling & Software 26 (2011) 711–722, http://dx.doi.org/10.1016/j.envsoft.2011.01.004.

[29] F. Montesano, A. Parente, P. Santamaria, Scientia Horticulturae 124 (2010) 338–344, http://dx.doi.org/10.1016/j.scienta.2010.01.017.

[30] F. Fornes, R.M. Belda, C. Carrión, V. Noguera, P. García-Agustín, M. Abad, Scientia Horticulturae 113 (2007) 52–59, http://dx.doi.org/10.1016/j.scienta.2007.01.008.

[31] C. Segura, C. Zaror, H.D. Mansilla, M.A. Mondaca, Journal of Hazardous Materials 150 (2008) 679–686, http://dx.doi.org/10.1016/j.jhazmat.2007.05.018.

[32] V. Kitsiou, N. Filippidis, D. Mantzavinos, I. Poulios, Applied Catalysis B: Environmental 86 (2009) 27–35, http://dx.doi.org/10.1016/j.apcatb.2008.07.018.

[33] M. Bourgin, F. Violleau, L. Debrauwer, J. Albet, Journal of Hazardous Materials 190 (2011) 60–68, http://dx.doi.org/10.1016/j.jhazmat.2011.02.065.

[34] R. Maciel, G.L. Sant'Anna Jr., M. Dezotti, Chemosphere 57 (2004) 711–719, http://dx.doi.org/10.1016/j.chemosphere.2004.07.032.

[35] E.M. Siedlecka, P. Stepnowski, Separation and Purification Technology 52 (2006) 317–324, http://dx.doi.org/10.1016/j.seppur.2006.05.014.

[36] E. Lipczynska-Kochany, G. Sprah, S. Harms, Chemosphere 30 (1995) 9–20, http://dx.doi.org/10.1016/0045-6535(94)00371-Z.

[37] J.J. Pignatello, Environmental Science & Technology 26 (1992) 944–951, http://dx.doi.org/10.1021/es00029a012.

[38] B.C. Faust, J. Hoigné, Atmospheric Environment Part A: General Topics 24 (1990) 79–89, http://dx.doi.org/10.1016/0960-1686(90)90443-Q.

[39] V. Kavitha, K. Palanivelu, Chemosphere 55 (2004) 1235–1243, http://dx.doi.org/10.1016/j.chemosphere.2003.12.022.

[40] N. Oturan, M. Zhou, M.A. Oturan, Journal of Physical Chemistry A 114 (2010) 10605–10611, http://dx.doi.org/10.1021/jp1062836.

[41] J.E. Grebel, J.J. Pignatello, W.A. Mitch, Environmental Science and Technology 44 (2010) 6822–6828.

[42] F.J. Millero, W. Yao, J. Aicher, Marine Chemistry 50 (1995) 21–39, http://dx.doi.org/10.1016/0304-4203(95)00024-L.

[43] A. Georgi, A. Schierz, U. Trommler, C.P. Horwitz, T.J. Collins, F. Kopinke, Applied Catalysis B: Environmental 72 (2007) 26–36, http://dx.doi.org/10.1016/j.apcatb.2006.10.009.

[44] D. Nichela, M. Haddou, F. Benoit-Marquié, M. Maurette, E. Oliveros, F.S. García Einschlag, Applied Catalysis B: Environmental 98 (2010) 171–179, http://dx.doi.org/10.1016/j.apcatb.2010.05.026.

[45] J. Šima, J. Makáňová, Coordination Chemistry Reviews 160 (1997) 161–189, http://dx.doi.org/10.1016/S0010-8545(96)01321-5.

[46] E.C. Constable, Metals and Ligand Reactivity, Ellis Horwood, New York, 1990.